TABLE I. Values of D_{ABC} (in atomic units)[a] for hydrogen–helium mixture.

	Semiempirical estimates[b]	Variational calculation[c]	Upper bound Eq. (7)
H–H–H	21.64	21.64	
He–He–He	1.47	1.47(1.49)[d]	
H–He–He	3.25	3.76(3.80)[d]	3.60
H–H–He	8.08	8.08(8.12)[d]	8.83

[a] 1 a.u. $=e^2a_0^5$.
[b] Reference 6.
[c] Reference 5.
[d] The value in parenthesis is scaled to correct for the calculated static polarizability error.

Using the Schwarz's Inequality,[3]

$$\left[\int_0^\infty f(x)g(x)\,dx\right]^2 \leq \int_0^\infty [f(x)]^2dx \int_0^\infty [g(x)]^2dx, \quad (3)$$

and Eq. (1), we obtain

$$C_{AB} \leq (C_{AA}C_{BB})^{1/2}. \quad (4)$$

This relation with the equal sign is often quoted as the "combining law"[4] and is usually derived from the London formula for dispersion energy by putting the same ionization energies for both Atoms A and B. Here it is seen that this law is actually an upper bound.

A more general inequality is the Hölder's relation[3]

$$\int_0^\infty |f(x)g(x)|dx \leq \left[\int_0^\infty |f(x)|^p dx\right]^{1/p}\left[\int_0^\infty |g(x)|^q dx\right]^{1/q}, \quad (5)$$

where p, $q>1$ and $(1/p)+(1/q)=1$. Since $\alpha_A(i\omega)$, $\alpha_B(i\omega)$, and $\alpha_C(i\omega)$ are positive functions, we can use the inequality (5) and write

$$\begin{aligned}
&\int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega)\alpha_C(i\omega)\,d\omega \\
&\leq \left\{\int_0^\infty [\alpha_A(i\omega)]^3 d\omega\right\}^{1/3}\left\{\int_0^\infty [\alpha_B(i\omega)\alpha_C(i\omega)]^{3/2} d\omega\right\}^{2/3} \\
&\leq \left\{\int_0^\infty [\alpha_A(i\omega)]^3 d\omega\right\}^{1/3}\left\{\left[\int_0^\infty [\alpha_B(i\omega)]^{3/2\times 2} d\omega\right]^{1/2}\right. \\
&\qquad \left.\times\left[\int_0^\infty [\alpha_C(i\omega)]^{3/2\times 2} d\omega\right]^{1/2}\right\}^{2/3} \\
&= \left\{\int_0^\infty [\alpha_A(i\omega)]^3 d\omega \int_0^\infty [\alpha_B(i\omega)]^3 d\omega \int_0^\infty [\alpha_C(i\omega)]^3 d\omega\right\}^{1/3}. \quad (6)
\end{aligned}$$

Thus, by Eq. (2), we have

$$D_{ABC} \leq (D_{AAA}D_{BBB}D_{CCC})^{1/3}. \quad (7)$$

To illustrate the usefulness of this relation, we present in Table I the upper bounds calculated from Eq. (7) for a mixture of hydrogen and helium atoms. There are two sets of calculations for this system, one with a variational method[5] and the other with a semiempirical method.[6] They agree with each other for all combinations except for the H–He–He interaction. The one calculated from the variational method falls outside the bound.

* Supported in part by a grant from the Research Corporation.
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Numerical One-Center Calculation of the ns–σ Rydberg Series of H_2^+

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(Received 6 May 1968)

We have calculated the energies and quantum defects for the lowest eight s–σ states of H_2^+ using the first-order perturbation theory. In zero-order, we retain only the spherical component of the core potential. The zero-order equation has previously been solved by Chen[1] for the lowest six s–σ states and his results for the ground state have been corrected by Cohen and Coulson,[2] and by Hauk and Parr.[3] The perturbation is simply the nonspherical part of the core potential, and its effects on the Rydberg orbital are included by solving the first-order perturbation equation. It is well known that such a procedure is not sufficient for the ground state[4]; however it is expected to be a better approximation for the highly excited Rydberg levels.[5] For these orbitals, the spherical component of the core potential plays a more dominant role in determining the eigenvalue.

The partial wave expansion of the core potential for H_2^+ is

$$-r_a^{-1}-r_b^{-1} = -2\sum_l (r_<^{2l}/r_>^{2l+1})\,P_{2l}(\cos\theta), \quad (1)$$

where $r_<=\min(R,r)$, $r_>=\max(R,r)$, and $2R(=2$ a.u.) is the internuclear separation. The zero-order equation for the ns–σ states is

$$[-\tfrac{1}{2}(d^2/dr^2)-(2/r_>)]\psi_n^0(r) = E_n^0\psi_n^0. \quad (2)$$

TABLE I. Perturbation energies for the ns–σ Rydberg series of H_2^+ at an internuclear separation of 2 a.u.

n	$-E_0$	$-E_2$	$-E_3$	$-E_t$	δ_n
1	1.018507	0.061408	0.016398	1.096313(1.10263)	0.3507
2	0.350367	0.007912	0.002218	0.360497(0.36087)	0.3554
3	0.174455	0.002396	0.000735	0.177586(0.17768)	0.3559
4	.0104041	0.001043	0.000339	0.105423	0.3556
5	0.068995	0.000538	0.000177	0.069710	0.3563
6	0.049069	0.000323	0.000110	0.049502	0.3563
7	0.036687	0.000203	0.000068	0.036958	0.3563
8	0.028456	0.000138	0.000047	0.028641	0.3564

If we expand the first-order wavefunction in the same form as the perturbation, the first-order equation decouples to give a separate equation for each partial wave of the form

$$\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{2l(2l+1)}{2r^2}-\frac{2}{r_>}-E_n^0\right)\psi_n^1(2l;r) = (2r_<^{2l}/r_>^{2l+1})\psi_n^0(r). \quad (3)$$

Both Eqs. (2) and (3) were solved by the matrix finite-difference method which we have discussed elsewhere.[6,7] The first-order wavefunction for the ground-state included partial waves up to $2l=16$ and the remaining states up to $2l=12$. The results for each level are given in Table I along with the exact values of the energy for the lowest three states.[8] In addition, the quantum defects δ_n were found from the formula

$$E_n=-Z_c^2/2(n+\delta_n)^2, \quad (4)$$

where Z_c is the charge on the core, and are listed in the last column. The contributions of the partial waves to the second-order energy are given in Table II for each excited state.

The results of Table I clearly show the rapid convergence of the perturbation energies for the higher Rydberg levels. Even for the third state, the energy agrees with the exact result better than 0.1%. On the other hand, from Table II we can see that the convergence of the partial wave expansion is about the same for each state. Within the accuracy of the numerical results (about five decimal places) the quantum defect has converged nicely to a limiting value of 0.356.

Because the method we have used is numerical, it should not be difficult to apply to a more general diatomic molecule. The charge distribution due to the core electrons can be determined from an appropriate two-center calculation and then expanded in a partial wave series in the same manner as the nuclear potential. The resulting zero- and first-order equations are very much like those we have solved here for H_2^+. A method which accounts for exchange effects and yet yields a local potential has been developed by Goddard[9] and thus would be particularly suited for numerical work. Another alternative is the use of a pseudopotential theory such as proposed by Hazi and Rice.[10] In any case, once a few of the higher levels have been deter-

TABLE II. Contribution of each partial wave to $-E_2$.

n \ $2l$	2	4	6	8	10	12
2	0.007034	0.000640	0.000150	0.000052	0.000023	0.000012
3	0.002125	0.000197	0.000047	0.000016	0.000007	0.000003
4	0.000922	0.000087	0.000020	0.000007	0.000003	0.000002
5	0.000477	0.000045	0.000011	0.000004	0.000002	0.000001
6	0.000285	0.000027	0.000006	0.000002	0.000001	0.000000_6
7	0.000180	0.000017	0.000004	0.000001	0.000000_6	0.0
8	0.000122	0.000012	0.000003	0.000001	0.0	0.0

mined, the energies can be fitted to a Rydberg formula and the remaining members of the series calculated.

* Contribution No. 3764.

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Errata

Erratum: Spectra and Structure of Mixed Organic Crystals

[J. Chem. Phys. **4,** 3612 (1968)]

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In the abstract, phenanthrene in naphthalene is stated to exhibit a multiplet structure, which is incorrect and evidently so from the context of the paper (cf., Sec. VI.D).

On p. 3617, paragraph 4, line 9, "shorter lifetime" should read "longer lifetime." The second line in the caption to Fig. 4 should be "The solid line is the approximate best line drawn through the calculated points (circles)." The unit of energy in Figs. 7 and 9 equals 100 cm^{-1}, and the calculated curves in Fig. 10 are for phenanthrene in naphthalene, *not* anthracene in biphenyl.

Erratum: Perimetric Coordinates

[J. Chem. Phys. **47,** 2229 (1967)]

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For the four-particle system, the set of 12 triangular conditions $r_1+r_2-r_{12}>0, r_1-r_2+r_{12}>0, -r_1+r_2+r_{12}>0$, etc., is not sufficient for the six numbers r_1, r_2, r_3, r_{12}, r_{23}, r_{31} to form the edges of a tetrahedron. It has recently been pointed out by Carter[1] that in addition to these conditions, they have to satisfy the following (tetrahedral) inequality:

$$r_1^2r_{23}^2(r_1^2+r_{23}^2-r_{12}^2-r_{13}^2)+r_2^2r_{13}^2(r_2^2+r_{13}^2-r_{12}^2-r_{23}^2)$$
$$+r_3^2r_{12}^2(r_3^2+r_{12}^2-r_{23}^2-r_{13}^2)+r_1^2r_2^2(r_{12}^2-r_{23}^2-r_{31}^2)$$
$$+r_2^2r_3^2(-r_{12}^2+r_{23}^2-r_{31}^2)+r_3^2r_1^2(-r_{12}^2-r_{23}^2+r_{31}^2)$$
$$+r_{12}^2r_{23}^2r_{31}^2\leq 0. \quad (1)$$

If we denote the set of points satisfying (1) by R, then the relative configuration of the four particles should be described by a point in a region $\bar{D}$ which is the intersection of R and the region D given in the original paper. It is still obviously true that there does not exist a nonsingular linear transformation which maps $\bar{D}$ onto D', the region in the u space characterized by $u_i\geq 0$ $(i=1, 2, \cdots, 6)$.

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